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(54) Title: METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS

(57) Abstract: This invention concerns a method for depositing transition metal nitride thin films by an Atomic Layer Deposition (ALD) type process. According to the method vapor-phase pulses of a metal source material, a reducing agent capable of reducing metal source material, and a nitrogen source material capable of reacting with the reduced metal source material are alternately and sequentially fed into a reaction space and contacted with the substrate. According to the invention as the reducing agent is used a boron compound which is capable of forming gaseous reaction byproducts when reacting with the metal source material.

## METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS

### Background of the Invention

#### 5 Field of the Invention

The present invention relates to metal nitride thin films. In particular, the invention concerns a method of growing tungsten nitride thin films by Atomic Layer Deposition (referred to as ALD hereinafter).

10

#### Description of Related Art

The integration level of components in integrated circuits is increasing, which rapidly brings about a need for a decrease of the size of components and interconnects. Design  
15 rules are setting the feature sizes to  $\leq 0.2 \mu\text{m}$ . Complete film coverage on deep bottoms and vias is hard to obtain.

Integrated circuits contain interconnects which are usually made of aluminium or copper. Especially copper is prone to diffusion to the surrounding materials. Diffusion affects the  
20 electrical properties of the circuits and active components may malfunction. The diffusion of metals from interconnects into active parts of the device is prevented with an electrically conductive diffusion barrier layer. Favored diffusion barriers are, e.g., amorphous transition metal nitrides, such as TiN, TaN and WN. The nitrides can be non-stoichiometric because nitrogen is located in interstitial position of the lattice.

25

In the Chemical Vapor Deposition method (referred to CVD hereinafter), the source materials are typically fed to reaction space together, and they react with each other when brought into contact with the substrate. It is also possible to feed one source material containing all desired reactant species to a CVD reactor, and heat it almost to a point where  
30 it decomposes thermally. When the heated gas contacts the substrate surface, a cracking reaction occurs and a film is grown. As is apparent from the above discussion, in CVD the concentration of the different source materials in the reaction space determines the growth of the film.

Atomic Layer Deposition (ALD) and, originally, Atomic Layer Epitaxy (ALE) is an advanced variation of CVD. The method name was changed from ALE into ALD to avoid possible confusion when discussing about polycrystalline and amorphous thin films. The ALD method is based on sequential self-saturated surface reactions. The method is described in detail in US Patents Nos. 4,058,430 and 5,711,811. The reactor design benefits from the usage of inert carrier and purging gases which makes the system fast.

The separation of source chemicals from each other by inert gases prevents gas-phase reactions between gaseous reactants and enables self-saturated surface reactions leading to film growth which requires neither strict temperature control of the substrates nor precise dosage control of source chemicals. Surplus chemicals and reaction byproducts are always removed from the reaction chamber before the next reactive chemical pulse is introduced into the chamber. Undesired gaseous molecules are effectively expelled from the reaction chamber by keeping the gas flow speeds high with the help of an inert purging gas. The purging gas pushes the extra molecules towards the vacuum pump used for maintaining a suitable pressure in the reaction chamber. ALD provides an excellent and automatic self-control for the film growth.

ALD has recently been used for depositing single layers of titanium nitride TiN (H. Jeon, J.W. Lee, J. H. Koo, Y. S. Kim, Y. D. Kim, D. S. Kim, "A study on the Characteristics of TiN Thin Film Deposited by Atomic Layer Chemical Vapor Deposition method", AVS 46<sup>th</sup> International Symposium, abstract TF-MoP17, <http://www.vacuum.org/symposium/seattle/technical.html>, to be presented October 27, 1999 in Seattle, USA).

According to Hiltunen et al. NbN, TaN, Ta<sub>3</sub>N<sub>5</sub>, MoN and Mo<sub>2</sub>N can be grown by ALD using metal halogenides as source chemicals (L. Hiltunen, M. Leskelä, M. Mäkelä, L. Niinistö, E. Nykänen, P. Soininen, "Nitrides of Titanium, Niobium, Tantalum and Molybdenum Grown as Thin Films by the Atomic Layer Epitaxy Method", Thin Solid Films, 166 (1988) 149 – 154). The use of additional zinc vapour during the deposition has decreased the resistivity of the nitride film either by increasing the metal / nitrogen ratio or by removing oxygen from the films.

J. W. Klaus has disclosed a process for growing tungsten nitride films using an ALD method (J.W. Klaus, "Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Sequential Surface Reactions", AVS 46<sup>th</sup> International Symposium, abstract TF-TuM6, <http://www.vacuum.org/symposium/seattle/technical.html>, to be presented October 26, 1999 in Seattle, USA). In the process of the publication, tungsten nitride  $W_2N$  is grown from  $WF_6$  and  $NH_3$ .

In the art, tungsten compounds have been reduced by using hydrogen ( $H_2$ ) (US Patent No. 5,342,652 and EP-A2-899 779), silanes, such as  $SiH_4$  (US Patent No. 5,691,235) and chlorosilanes, such as  $SiHCl_3$  (US Patent No. 5,723,384).

There are, however, drawbacks related to these prior art methods. Silanes may also react with  $WF_6$ , thus forming tungsten silicides, such as  $WSi_2$ . Hydrogen can reduce a tungsten compound into tungsten metal which has too low vapor pressure for being transported in gas phase onto substrates. Traditional CVD processes may leave significant amounts of impurities in thin films, especially at low deposition temperatures.

#### Summary of the Invention

It is an object of the present invention to eliminate the problems of the prior art and to provide a novel method of depositing transition metal nitride thin films by an ALD type process. It is a further object of the invention to provide a process for preparing diffusion barriers on metal surfaces in integrated circuits.

The invention is based on the surprising finding that by feeding into a reactor chamber, which contains a substrate, a suitable transition metal compound and, a reducing boron compound pulse and a nitrogen compound, a metal nitride film with low resistivity can be grown. According to the present invention, the reaction between the gaseous boron compound and the metal species reduces the metal compound and gives rise to gaseous reaction byproducts, which easily can be removed from the reaction space.

According to a preferred embodiment of the invention, the metal nitride thin films are grown by an ALD type process. This is carried out by sequentially feeding into a reactor chamber, which contains a substrate, alternate pulses of a suitable transition metal compound, a reducing boron compound pulse and a nitrogen compound, said boron

compound and said nitrogen compound being fed after the metal compound. Thus, a metal nitride film with low resistivity can be grown in accordance with the principles of ALD method. According to the present invention, the reaction between the gaseous boron compound and the metal species bound to the surface reduces the metal compound and  
5 gives rise to gaseous reaction byproducts, which easily can be removed from the reaction space.

A diffusion barrier can be grown in an integrated circuit by depositing, during the manufacture of the integrated circuit, a metal nitride thin film on a dielectric surface or a  
10 metal surface present on the silicon wafer blank.

More specifically, the present method is characterized by what is stated in the characterizing part of claim 1.

15 The process for preparing diffusion barriers is characterized by what is stated in the characterizing part of claim 20.

A number of considerable advantages are achieved with the aid of the present invention. Metal nitride thin films, in particular tungsten nitride thin films, can be grown at low  
20 temperatures. The boron compounds used as source materials are easy to handle and vaporise.

As mentioned above, the boron compounds formed as byproducts of the reaction between the metal species and the reducing boron compound are essentially gaseous and they exit  
25 the reactor easily when purging with an inert gas. The boron residues in the film are on a very low level, typically below 5 wt-%, preferably 1 wt-% or less and in particular 0.5 wt-% or less. The resistivity of the film is low. The growing rate of the film is acceptable. Also the reaction times are short, and in all it can be said that films can be grown very effectively by means of the present process.

30

The film grown with the present process exhibits good thin films properties. Thus, especially the metal nitride films obtained by an ALD type process have an excellent conformality even on uneven surfaces and on trenches and vias. The method also provides an excellent and automatic self-control for the film growth.

The metal nitride thin films grown by the present invention can be used, for example, as ion diffusion barrier layers in integrated circuits. Tungsten nitride stops effectively oxygen and increases the stability of metal oxide capacitors. Transition metal nitrides and especially tungsten nitride is also suitable as an adhesion layer for a metal, as a thin film resistor, for stopping the migration of tin through via holes and improving the high-temperature processing of integrated circuits.

Next, the invention is described in detail with the aid of the following detailed description and by reference to the attached drawing.

### **Brief Description of the Drawing**

Figure 1 presents a block diagram of a pulsing sequence according to a preferred embodiment of the invention.

### **Detailed Description of the Invention**

#### **Definitions**

20

For the purposes of the present invention, a "chemical gaseous deposition process" designates a deposition process in which the reactants are fed to a reaction space in vapor phase. Examples of such processes include CVD and ALD.

25 For the purposes of the present invention, an "ALD type process" designates a process in which deposition of vaporized material onto a surface is based on sequential self-saturating surface reactions. The principle of ALD process is disclosed, e.g., in US 4 058 430.

"Reaction space" is used to designate a reactor or reaction chamber in which the conditions can be adjusted so that the deposition by ALD is possible.

"Thin film" is used to designate a film which is grown from elements or compounds that are transported as separate ions, atoms or molecules via vacuum, gaseous phase or liquid phase from the source to the substrate. The thickness of the film depends on the application

and it varies in a wide range, e.g., from one molecular layer to 800 nm, even up to 1000 nm.

### The deposition process

5

According to the present invention, metal nitride thin films are prepared by ALD type process.

10

According to CVD process, a film is grown on a substrate placed in a reaction chamber at elevated temperatures. The principles of CVD are well known to those skilled in the art. The metal source material, the nitrogen source material and the reducing boron compound are typically fed to the reaction space essentially simultaneously, although the duration of the pulsing of the different species may vary. It is also possible to feed a source material comprising both the nitrogen and metal to the reaction space together with the reducing boron compound.

15

According to the present invention, metal nitride thin films are prepared by the ALD process. Thus, a substrate placed in a reaction chamber is subjected to sequential, alternately repeated surface reactions of at least two vapor-phase reactants for the purpose of growing a thin film thereon. Metal compounds used as source materials are reduced by boron compounds on a substrate maintained at an elevated temperature. The boron compounds, on the other hand, are not incorporated into the film. The reduced metal species react on the surface with gaseous or volatile nitrogen source material.

20

The conditions in the reaction space are adjusted so that no gas-phase reactions, i.e., reactions between gaseous reactants, occur, only surface reactions, i.e., reactions between species adsorbed on the surface of the substrate and a gaseous reactant. Thus, the molecules of the reducing boron compound react with the deposited metal source compound layer on the surface, and the nitrogen source material reacts with the reduced metal compound on the surface.

25  
30

According to the present process the vapor-phase pulses of the metal source material and the reducing agent are alternately and sequentially fed to the reaction space and contacted with the surface of the substrate fitted into the reaction space. The "surface" of the

substrate comprises initially the surface of the actual substrate material which optionally has been pretreated in advance, e.g., by contacting it with a chemical for modifying the surface properties thereof. During the growing of the thin films, the previous metal nitride layer forms the surface for the following metal nitride layer. The reagents are preferably  
5 fed into the reactor with the aid of an inert carrier gas, such as nitrogen.

Preferably, and to make the process faster, the metal source material pulse, the reducing boron compound pulse and the nitrogen source material pulse are separated from each other by an inert gas pulse, also referred to as gas purge in order to purge the reaction space  
10 from the unreacted residues of the previous chemical. The inert gas purge typically comprises an inactive gas, such as nitrogen, or a noble gas, such as argon.

Thus, one pulsing sequence (also referred to as a "cycle") preferably consists essentially of

- 15 - feeding a vapor-phase pulse of a metal source chemical with the help of an inert carrier gas into the reaction space;
- purging the reaction space with an inert gas;
- feeding a vapor-phase pulse of a boron source chemical with the help of an inert carrier gas into the reaction space;
- purging the reaction space with an inert gas;
- 20 - feeding a vapor-phase pulse of a nitrogen source material into the reaction space; and
- purging the reaction space with an inert gas;

The purging time is selected to be long enough to prevent gas phase reactions and to  
25 prevent transition metal nitride thin film growth rates higher than one lattice constant of said nitride per cycle.

The deposition can be carried out at normal pressure, but it is preferred to operate the method at reduced pressure. The pressure in the reactor is typically 0.01 – 20 mbar, preferably 0.1 – 5 mbar. The substrate temperature has to be low enough to keep the bonds  
30 between thin film atoms intact and to prevent thermal decomposition of the gaseous reactants. On the other hand, the substrate temperature has to be high enough to keep the source materials in gaseous phase, i.e., condensation of the gaseous reactants must be avoided. Further, the temperature must be sufficiently high to provide the activation energy

for the surface reaction. Depending on the reactants and the pressure the temperature of the substrate is typically 200 – 700 °C, preferably 250 – 500 °C.

At these conditions, the amount of reactants bound to the surface will be determined by the surface. This phenomenon is called "self-saturation".

Maximum coverage on the substrate surface is obtained when a single layer of metal source chemical molecules is adsorbed. The pulsing sequence is repeated until a metal nitride film of predetermined thickness is grown.

10

The source temperature is preferably set below the substrate temperature. This is based on the fact that if the partial pressure of the source chemical vapor exceeds the condensation limit at the substrate temperature, controlled layer-by-layer growth of the film is lost.

15 The amount of time available for the self-saturated reactions is limited mostly by the economical factors such as required throughput of the product from the reactor. Very thin films are made by relatively few pulsing cycles and in some cases this enables an increase of the source chemical pulse times and, thus, utilization of the source chemicals with a lower vapor pressure than normally.

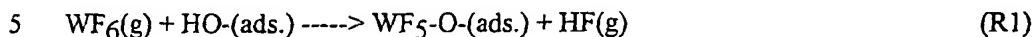
20

The substrate can be of various types. Examples include silicon, silica, coated silicon, copper metal, and various nitrides, such as metal nitrides. Conventionally, the preceding thin film layer deposited will form the substrate surface for the next thin film.

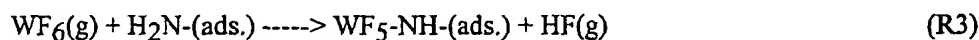
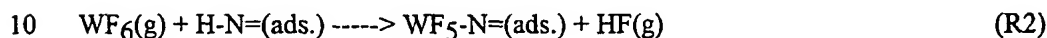
25 The present method provides for growing of conformal layers in geometrically challenging applications. As mentioned above, it is possible to produce diffusion barriers on dielectric (e.g. silica or nitride) or metal (e.g. copper) surfaces in integrated surfaces. In these cases, said surfaces form the substrates for the growing of the metal nitride thin films.

30 The metal source material can attach on a nitride surface more easily if there are certain active groups on the surface. In the following is presented suggested reaction equations of tungsten hexafluoride ( $WF_6$ ) for the attaching to silicon wafers.

Silicon wafers have a native oxide on top. The silica ( $\text{SiO}_2$ ) layer may be just a few molecular layers thick. On a silica surface there are "-OH" groups which can serve as reactive surface sites.

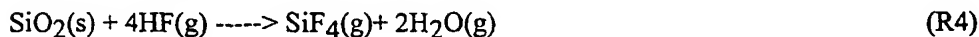


During the growth process, the metal source compound attaches to the nitride surface. Suggested reaction equations for  $\text{WF}_6$  are presented in R2 and R3.



It is of importance that the process parameters are carefully optimised to protect silicon wafer against corrosion especially during the first phase of the nitride growth, since the evolved HF gas can attack silica and form volatile silicon tetrafluoride.

15



The uncovered silicon is prone to further, undesired, reactions.

20

The metal source materials most typically used are volatile or gaseous compounds of transition metals, i.e., elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and/or 12 (according to the system recommended by IUPAC) in the periodic table of elements. In particular, the film consists essentially of W, Ti, Zr, Hf, V, Nb, Ta, Cr and/or Mo nitride(s) and thus gaseous or volatile compounds of these are preferably used in the method of the present invention.

25

Since the properties of each metal compound vary, the suitability of each metal compound for the use in the process of the present invention has to be considered. The properties of the compounds are found, e.g., in N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, 1<sup>st</sup> edition, Pergamon Press, 1986.

30

The metal source material (as well as the reducing boron compound and the nitrogen source material) has to be chosen so that the requirements for sufficient vapor pressure, the

above-discussed criteria of sufficient thermal stability at substrate temperature and sufficient reactivity of the compounds are fulfilled.

5 Sufficient vapor pressure means that there must be enough source chemical molecules in the gas phase near the substrate surface to enable fast enough self-saturated reactions at the surface.

10 In practice, sufficient thermal stability means that the source chemical itself must not form growth-disturbing condensable phases on the substrates or leave harmful levels of impurities on the substrate surface through thermal decomposition. Thus, one aim is to avoid non-controlled condensation of molecules on substrates.

Further selecting criteria include the availability of the chemical at high purity, and the ease of handling, inter al., without severe precautions.

15

Typically, suitable metal source materials can be found among halides, preferably fluorides, chlorides, bromides or iodides, or metal organic compounds, preferably alkylaminos, cyclopentadienyls, dithiocarbamates or betadiketonates of desired metal(s).

20 According to a preferred embodiment of the invention, tungsten nitride ( $W_xN_y$ , referred to as WN hereinafter) is grown. Then, tungsten source chemical is a tungsten compound selected according to the above criteria. Preferably, the tungsten source material is selected from the group comprising

- 25 – a halide such as  $WF_x$ ,  $WCl_y$ ,  $WBr_m$  or  $WI_n$  wherein x, y, m and n are integers from 1 to 6, in particular  $WF_6$ ;
- a carbonyl such as tungsten hexacarbonyl  $W(CO)_6$  or tricarbonyl(mesitylene)tungsten;
- cyclopentadienyl such as bis(cyclopentadienyl)tungsten dihydride, bis(cyclopentadienyl)tungsten dichloride or bis(cyclopentadienyl)ditungsten
- 30 hexacarbonyl; and
- $\beta$ -diketonate.

According to a preferred embodiment transition metal nitrides are mixed so that in the growing process two or more different metal source materials are used. For example, tungsten nitride can be mixed with TiN.

- 5 The metal reactant will react with the substrate surface forming a (covalent) bond to the surface bonding groups. The adsorbed metal species will contain a residue of the reactant compound, such as halogen or hydrocarbon. According to the present invention, this residue reacts with the gaseous boron compound, which reduces the metal compound on the surface.

10

- The reducing strengths of the boron compounds vary. Thus, some boron compounds may reduce the metal compound to elemental metal, and others to a certain oxidation state. It is important that only those metals which are reactive with the nitrogen compounds also in their elemental form are reduced to metals. Typically, the oxidation state of the metal source compound is reduced so that the metal on the surface is in a form of a compound. The metal compounds react with the nitrogen source materials easily forming metal nitrides.

- 20 The boron sources are selected bearing in mind the same criteria as for the metal source materials. In general, the boron compound can be any volatile, thermally sufficiently stable and reactive boron compound capable of reducing the metal species bonded to the surface.

- 25 The reactions of different metal source materials with one and same reducing agent (and vice versa) can lead to different reaction (by)products. According to the present invention, the metal source material and boron compound are selected so that the resulting boron compound(s) is (are) gaseous. By this is meant that the compound formed is gaseous enough to be moved from the reaction space with the aid of the inert purging gas, and, on the other hand, does not decompose, e.g., catalytically or thermally, to condensable species. In all, byproducts will not remain as impurities in the films. If a reactive site on the surface is contaminated, the growing rate of the film decreases. By selecting the metal source material(s) and boron compound as indicated above, the growing rate of the film does not essentially decrease, i.e., decreases by a maximum of 0.1%, preferably by less than 0.01%, and in particular by less than 0.001% in each cycle. An example of an unsuitable pair is  $\text{TiCl}_4$  and triethyl boron, the reaction thereof not leading to desired results.

The selection can be facilitated with computer programs having a sufficiently extensive thermodynamics database, which enables to check the reaction equilibrium and thus predict which reactants have thermodynamically favorable reactions. An example of this kind of  
5 programs is HSC Chemistry, version 3.02 (1997) by Outokumpu Research Oy, Pori, Finland.

A vast range of boron chemicals makes it possible to choose suitable reducing strength and avoid boride formation. It is possible to use one or more boron compounds in the growing  
10 of one and same thin film.

Preferably, one or more of the following boron compounds is used:

Boranes having formula (I)

15



wherein  $n$  is an integer from 1 to 10, preferably from 2 to 6, and  
 $x$  is an even integer, preferably 4, 6 or 8,

20 or formula (II)



(II)

wherein  $n$  is an integer from 1 to 10, preferably from 2 to 6, and  
 $m$  is an integer different than  $n$ ,  $m$  being from 1 to 10, preferably from 2 to 6.

25

Boranes according to formula (I) are exemplified by *nido*-boranes ( $B_nH_{n+4}$ ), *arachno*-boranes ( $B_nH_{n+6}$ ) and *hypho*-boranes ( $B_nH_{n+8}$ ). Of the boranes according to formula (II), examples include *conjuncto*-boranes ( $B_nH_m$ ). Also borane complexes, such as  
( $CH_3CH_2$ )<sub>3</sub>N·BH<sub>3</sub> can be used.

30

Borane halides, particularly fluorides, bromides and chlorides. As an example of a suitable compound B<sub>2</sub>H<sub>5</sub>Br should be mentioned. It is also possible to use borane halide complexes

35

Boron halides with high boron/halide ratio, such as  $B_2F_4$ ,  $B_2Cl_4$  and  $B_2Br_4$ .

Halogenoboranes according to formula (III)



wherein X is Cl or Br and

$n = 4, 8-12$  when  $X = Cl$ , and

$n = 7-10$  when  $X = Br$

10 Carboranes according to formula (IV)



wherein  $n$  is an integer from 1 to 10, preferably from 2 to 6, and

$x$  is an even integer, preferably 2, 4 or 6.

15 Examples of carboranes according to formula (IV) include *closo*-carboranes ( $C_2B_nH_{n+2}$ ), *nido*-carboranes ( $C_2B_nH_{n+4}$ ), and *arachno*-carboranes ( $C_2B_nH_{n+6}$ ).

Amine-borane adducts according to formula (V)



wherein R is linear or branched  $C_1 - C_{10}$ , preferably  $C_1 - C_4$  alkyl or H, and

X is linear or branched  $C_1 - C_{10}$ , preferably  $C_1 - C_4$  alkyl, H or halogen,

Aminoboranes where one or more of the substituents on B is an amino group according

25 formula (VI)



wherein R is linear or branched  $C_1 - C_{10}$ , preferably  $C_1 - C_4$  alkyl or substituted or unsubstituted aryl group.

30 An example of suitable aminoborane is  $(CH_3)_2NB(CH_3)_2$ .

Cyclic borazine  $(-BH-NH-)_3$  and its volatile derivatives.

Alkyl borons or alkyl boranes, wherein the alkyl is typically linear or branched  $C_1 - C_{10}$  alkyl, preferably  $C_2 - C_4$  alkyls. Particularly preferred is triethyl boron  $(CH_3CH_2)_3B$ , because it is easily vaporized.

- 5 Particularly preferred boron compound is triethyl boron  $(CH_3CH_2)_3B$ .

The reduced metal species bound on the substrate surface will then be subjected to reaction with a nitrogen-containing compound. The nitrogen compound used as the nitrogen source material is volatile or gaseous and chosen according to the above criteria, including the  
10 criterion relating to the reaction byproducts.

Preferably, the nitrogen compound is selected from the group comprising

- ammonia ( $NH_3$ ) and its salts, preferably halide salt, in particular ammonium fluoride or ammonium chloride;
- 15 - hydrogen azide ( $HN_3$ ) and the alkyl derivatives of the said compound such as  $CH_3N_3$ ;
- hydrazine ( $N_2H_4$ ) and salts of hydrazine such as hydrazine hydrochloride;
- alkyl derivatives of hydrazine such as dimethyl hydrazine;
- nitrogen fluoride  $NF_3$ ;
- 20 - hydroxyl amine ( $NH_2OH$ ) and its salts such as hydroxylamine hydrochloride;
- primary, secondary and tertiary amines such as methylamine, diethylamine and triethylamine; and
- nitrogen radicals such as  $NH_2^*$ ,  $NH^{**}$  and  $N^{***}$ , wherein \* means a free electron capable of bonding, and excited state of nitrogen ( $N_2^*$ ).

25

When no reducing agent is used, the nitride film resulting from the above-described process has a N/W molar ratio of greater than 1, i.e., the nitride is mostly in the form  $WN_2$ . When operating without a reducing agent, it is also possible to feed the nitrogen source material pulse into the reaction space first and the transition metal source material second,  
30 i.e., use a reverse order of source material pulses. The deposition process ends also in this case with a nitrogen source material pulse. Thus, the structure of the film is different from the one obtained by a process otherwise similar but employing a reducing agent. The film produced according to the process employing no reducing agent, has rather high resistivity.

The following non-limiting examples illustrate the invention.

#### EXAMPLE 1

- 5 Tungsten hexafluoride ( $\text{WF}_6$ ) and ammonia ( $\text{NH}_3$ ) were used as source chemicals. Both chemicals are liquefied gases at room temperature and poses high enough vapor pressure without additional heating for the ALD process. Source tubing and the reactor were purged with nitrogen gas which had a purity of 99.9999% (i.e. 6.0). The  $\text{N}_2$  gas was prepared from liquid nitrogen. A 200-mm silicon wafer was loaded to an ALD reactor as described in
- 10 Finnish Patent No. 100409 of assignee. Source chemicals were pulses alternately to the substrates at the reaction chamber. The deposition was started and ended with an  $\text{NH}_3$  pulse. The pulsing cycle consisted of the following steps:

- $\text{NH}_3$  vapor pulse 0.5 s
- 15  $\text{N}_2$  gas purge 1.0 s
- $\text{WF}_6$  vapor pulse 0.25 s
- $\text{N}_2$  purge 0.8 s

- The pulsing cycle was repeated for 500 times which produced a 30 nm film with the typical
- 20 growth rate of 0.6 Å/cycle. The composition, impurities and the thickness of the resulting thin film were analyzed by Electron Diffraction Spectroscopy (referred to as EDS hereinafter). EDS showed an N/W ratio of 1.3 which means that the phase of tungsten nitride was between WN and  $\text{WN}_2$ , i.e. rich in nitrogen. Decreasing the growth temperature from 400 °C to 360 °C increased the fluorine content from 2 wt.-% to 4 wt.-%.

25

The resistivity of the tungsten nitride film was obtained by combining the thickness value with the four-point probe measurements. The resistivity of the film grown at 400 °C was 1900  $\mu\Omega\text{cm}$ . High resistivity was possibly caused by the high nitrogen content of the film.

#### 30 EXAMPLE 2

Tungsten hexafluoride ( $\text{WF}_6$ ), triethylboron ( $(\text{CH}_3\text{CH}_2)_3\text{B}$ ) and ammonia ( $\text{NH}_3$ ) were used as source chemicals. All the chemicals are liquids or liquefied gases at room temperature and poses high enough source vapor pressure without additional heating for the ALD

process. Source tubing and the reactor were purged with nitrogen gas which had a purity of 99.9999% (i.e. 6.0). The  $N_2$  gas was prepared from liquid nitrogen. A 200-mm silicon wafer was loaded to an F200 ALD reactor. Source chemicals were pulses alternately to the substrates at the reaction chamber. The pulsing cycle consisted of the following steps:

5

WF<sub>6</sub> vapor pulse 0.25 s

$N_2$  purge 0.8 s

(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>B vapor pulse 0.01 s

$N_2$  gas purge 0.5 s

10 

NH<sub>3</sub> vapor pulse 0.25 s

$N_2$  gas purge 0.5 s

The pulsing cycle was repeated for 500 times resulting in a 30-nm film at 360 °C. The samples were analyzed by EDS for thickness and composition. The thin film consisted of tungsten and nitrogen while boron could not be seen in detectable amounts. There was 3 wt.-% of fluorine as an impurity in the film. The resistivity of the tungsten nitride film was obtained by combining the thickness value with the four-point probe measurements. The resistivities were 130 - 160  $\mu\Omega\text{cm}$ .

20 The inventors assume that the boron chemical acted as a reducing agent and removed fluorine from tungsten fluoride. The benefit of this boron chemical is that possible byproducts such as BF<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>F are gaseous at the deposition temperature and do not disturb the nitride growth.

## Claims:

1. A method of growing metal nitride thin film on a substrate by an Atomic Layer Deposition (ALD) type process, wherein vapour-phase pulses of
  - 5       – a metal source material,
  - a reducing agent capable of reducing the metal source material, and
  - a nitrogen source material capable of reacting with the reduced metal source material,are alternately and sequentially fed into a reaction space and contacted with the substrate,
  - 10   characterized by
    - using as the reducing agent a boron compound which is capable of forming gaseous reaction by-products when reacting with the metal source material.
2. The method according to claim 1, wherein the reducing agent is capable of forming
  - 15   gaseous reaction by-products when reacting with the metal source material bound to the surface.
3. The method according to claim 1 or 2, wherein the pulsing cycle consists essentially of the steps of
  - 20       – feeding a vapor-phase pulse of metal source chemical with the help of an inert carrier gas into the reaction space;
  - purging the reaction space with an inert gas;
  - feeding a vapor-phase pulse of a boron source chemical with the help of an inert carrier gas into the reaction space;
  - 25       – purging the reaction space with an inert gas;
  - feeding a vapor-phase pulse of the nitrogen source chemical into the reaction space; and
  - purging the reaction space with an inert gas.
- 30   4. The method according to any of claims 1 - 3, wherein the metal in the metal source materials is selected from the group comprising W, Mo, Cr, Ta, Nb, V, Hf, Zr and Ti.
5. The method according to claim 4, wherein the metal compound in the metal source

material is selected from the group comprising halides, preferably fluorides, chlorides, bromides or iodides, and metal organic compounds, preferably alkylaminos, cyclopentadienyls, dithiocarbamates or betadiketonates.

- 5 6. The method according to claim 4 or 5, wherein the metal source material is a tungsten compound selected from the group comprising
- tungsten halides, preferably  $WF_x$ ,  $WCl_y$ ,  $WBr_m$  or  $WI_n$  wherein x, y, m and n are integers from 1 to 6, in particular  $WF_6$ ;
  - tungsten carbonyls, preferably tungsten hexacarbonyl  $W(CO)_6$  or
  - 10 tricarbonyl(mesitylene)tungsten;
  - tungsten cyclopentadienyls such as bis(cyclopentadienyl)tungsten dihydride, bis(cyclopentadienyl)tungsten dichloride or bis(cyclopentadienyl)ditungsten hexacarbonyl; and
  - tungsten  $\beta$ -diketonate.

15

7. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising boranes of formula (I)



- 20 wherein n is an integer from 1 to 10, preferably from 2 to 6, and  
x is an even integer, preferably 4, 6 or 8,

and formula (II)



- wherein n is an integer from 1 to 10, preferably from 2 to 6, and  
25 m is an integer different than n, m being from 1 to 10, preferably from 2 to 6, and complexes thereof.

8. The method according to claim 7, wherein the boranes are selected from the group comprising *nido*-boranes of formula  $B_nH_{n+4}$ , *arachno*-boranes of formula  $B_nH_{n+6}$ , *hypho*-  
30 boranes of formula  $B_nH_{n+8}$  and *conjuncto*-boranes  $B_nH_m$ , wherein n and m are the same as in claim 6.

9. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising carboranes according to formula (IV)



wherein  $n$  is an integer from 1 to 10, preferably from 2 to 6, and  
 $x$  is an even integer, preferably 2, 4 or 6.

- 5 10. The method according to claim 9, wherein the carboranes are selected from the group comprising *closo*-carboranes ( $C_2B_nH_{n+2}$ ), *nido*-carboranes ( $C_2B_nH_{n+4}$ ) and *arachno*-carboranes ( $C_2B_nH_{n+6}$ ), wherein  $n$  is the same as in claim 8.

11. The method according to any of claims 1 - 6, wherein the boron compound is selected  
 10 from the group comprising amine-borane adducts according to formula (V)



wherein  $R$  is linear or branched  $C_1 - C_{10}$ , preferably  $C_1 - C_4$  alkyl or H, and  
 $X$  is linear or branched  $C_1 - C_{10}$ , preferably  $C_1 - C_4$  alkyl, H or halogen.

- 15 12. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising aminoboranes where one or more of the substituents on B is an amino group according formula (VI)



- wherein  $R$  is linear or branched  $C_1 - C_{10}$ , preferably  $C_1 - C_4$  alkyl or substituted or  
 20 unsubstituted aryl group.

13. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising alkyl borons and alkyl boranes, wherein the alkyl is linear or branched  $C_1 - C_{10}$  alkyl, preferably  $C_2 - C_4$  alkyl.

25

14. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising boron halides having a high boron/halide ratio, preferably  $B_2F_4$ ,  $B_2Cl_4$  and  $B_2Br_4$ .

- 30 15. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising halogenoboranes of formula (III)

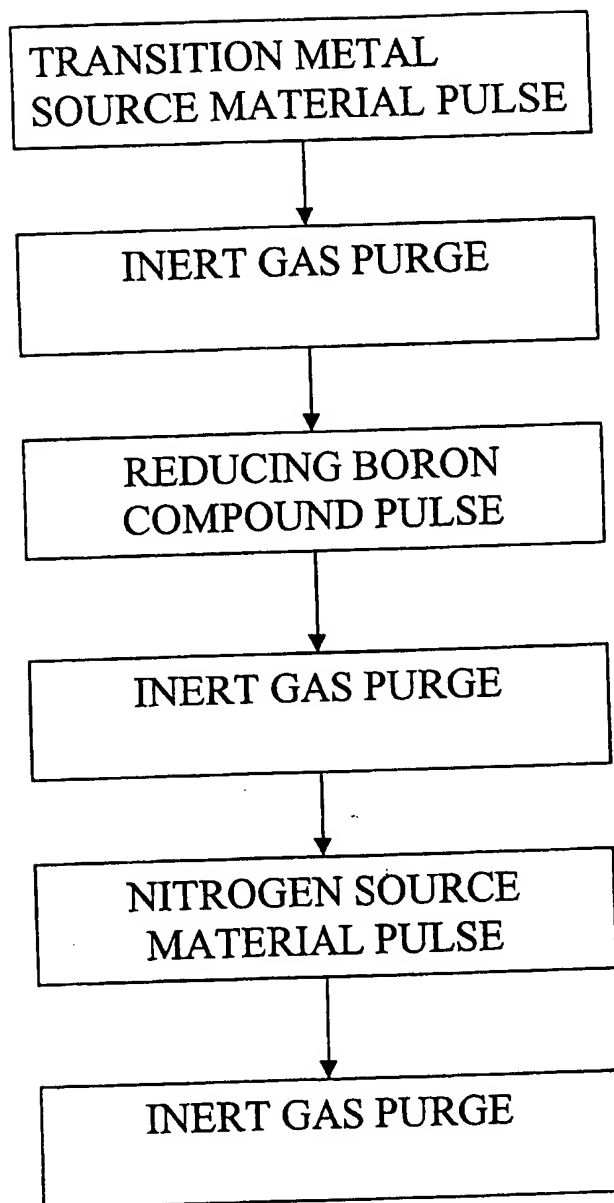


wherein  $X$  is Cl or Br and  
 $n = 4, 8-12$  when  $X = Cl$ , and

n = 7-10 when X = Br.

16. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising cyclic borazine ( $-\text{BH}-\text{NH}-$ ), and the volatile derivatives thereof.
- 5
17. The method according to any of claims 1 - 6, wherein the boron compound is selected from the group comprising borane halides and complexes thereof.
18. The method according to any of the preceding claims, wherein the nitrogen source
- 10 material is selected from the group comprising
- ammonia ( $\text{NH}_3$ ) and its salts, preferably halide salt, in particular ammonium fluoride or ammonium chloride;
  - hydrogen azide ( $\text{HN}_3$ ) and the alkyl derivatives thereof, preferably  $\text{CH}_3\text{N}_3$ ;
  - hydrazine ( $\text{N}_2\text{H}_4$ ) and salts of hydrazine such as hydrazine hydrochloride;
  - 15 - alkyl derivatives of hydrazine, preferably dimethyl hydrazine;
  - nitrogen fluoride  $\text{NF}_3$ ;
  - hydroxyl amine ( $\text{NH}_2\text{OH}$ ) and salts thereof, preferably hydroxylamine hydrochloride;
  - primary, secondary and tertiary amines, preferably methylamine, diethylamine and
  - 20 triethylamine; and
  - nitrogen radicals such as  $\text{NH}_2^*$ ,  $\text{NH}^{**}$ ,  $\text{N}^{***}$ , wherein \* is a free electron capable of bonding, and excited state of nitrogen ( $\text{N}_2^*$ ).
19. The method according to any of the preceding claims, wherein the substrate is selected
- 25 from the group comprising silicon, silica, coated silicon, copper metal, and nitrides.
20. Process for preparing a diffusion barrier in an integrated circuit, comprising depositing during the manufacture of the integrated circuit a metal nitride thin film on a dielectric surface or a metal surface of the integrated circuit by a method in accordance with any of
- 30 the claims 1 - 19.
21. The use of a boron compound according to any of claims 7-17 as a reducing agent for growing transition metal nitride thin films by an ALD type process.

1/1

**Fig 1**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00895

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C23C 16/44, C23C 16/00, C30B 25/02, H05K 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, C30B, H01L, H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	J. ELECTROCHEMICAL SOCIETY, Volume 142, No 8, August 1995, Mikko Ritala et al, "Atomic Layer Epitaxy Growth of TiN Thin Films" page 2731 ~ page 2737  --	1-21
A	APPLIED SURFACE SCIENCE, Volume 82/83, 1994, Kai-Erik Elers et al, "NbC15 as a precursor in atomic layer epitaxy", page 468 - page 474, see especially page 469 - 471 and 473  --	1-21

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

16 January 2001

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 00/00895

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>JP 8264530 A (FUJITSU LTD) 1996-10-11 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 2001-01-16). Retrieved from: EPO WPI Database. DW199651, Accession No. 1996-511211; &amp; JP 8264530 (FUJITSU LTD) 1997-02-28 (abstract). (online)(retrieved on 2001-01-16). Retrieved from: EPO PAJ Database</p> <p style="text-align: center;">-- -----</p>	1-21

POWERED BY **Dialog****Basic Patent (Number,Kind,Date):** FI 200000564 A0 20000310**Patent Family:**

Patent Number	Kind	Date	Application Number	Kind	Date
AU 200068003	A5	20010319	AU 200068003	A	20000824
AU 200079257	A5	20010423	AU 200079257	A	20001012
AU 200079268	A5	20010423	AU 200079268	A	20001013
AU 200110884	A5	20010430	AU 200110884	A	20001016
AU 200112082	A5	20010430	AU 200112082	A	20001016
FI 9902233	A	20010416	FI 992233	A	19991015
FI 9902234	A	20010416	FI 992234	A	19991015
FI 9902235	A	20010416	FI 992235	A	19991015
FI 200000564	A	20010416	FI 2000564	A	20000310
FI 200000564	A0	20000310	FI 2000564	A	20000310 (Basic)
WO 200115220	A1	20010301	WO 2000US23252	A	20000824
WO 200127346	A1	20010419	WO 2000FI884	A	20001012
WO 200127347	A1	20010419	WO 2000FI895	A	20001013
WO 200129280	A1	20010426	WO 2000US28537	A	20001016
WO 200129891	A1	20010426	WO 2000US23213	A	20000824
WO 200129893	A1	20010426	WO 2000US28654	A	20001016

**Priority Data:**

Patent Number	Kind	Date
US 150486	P	19990824
US 159799	P	19991015
US 176944	P	20000118
WO 2000US23252	W	20000824
FI 992233	A	19991015
WO 2000FI884	W	20001012
FI 992234	A	19991015
WO 2000FI895	W	20001013
FI 992235	A	19991015
FI 2000564	A	20000310
US 176948	P	20000118
WO 2000US28537	W	20001016
US 175799	P	19991015

## PATENT FAMILY:

## Australia (AU)

Patent (Number,Kind,Date): AU 200068003 A5 20010319  
METHOD FOR BOTTOMLESS DEPOSITION OF BARRIER LAYERS IN INTEGRATED CIRCUIT METALLIZATION SCHEMES (English)

Patent Assignee: ASM INC

Author (Inventor): SATTA ALESSANDRA; MAEX KAREN; ELMERS KAI-ERIK; SAANILA VILLE ANTERO; SOININEN PEKKA JUHA; HAUKKA SUVI P

Priority (Number,Kind,Date): US 150486 P 19990824; US 159799 P 19991015; US 176944 P 20000118; WO 2000US23252 W 20000824

Applic (Number,Kind,Date): AU 200068003 A 20000824

IPC: \* H01L-021/768; H01L-023/532; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(13)187114R; 134(21)304079W; 134(22)318948R

Derwent WPI Acc No: \* C 01-218475

Language of Document: English

Patent (Number,Kind,Date): AU 200079257 A5 20010423

METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS (English)

Patent Assignee: ASM MICROCHEMISTRY OY

Author (Inventor): ELMERS KAI-ERIK

Priority (Number,Kind,Date): FI 992233 A 19991015; WO 2000FI884 W 20001012

Applic (Number,Kind,Date): AU 200079257 A 20001012

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; C30B-035/00

CA Abstract No: \* 134(21)303341P; 134(21)304215N; 134(22)318948R

Language of Document: English

Patent (Number,Kind,Date): AU 200079268 A5 20010423

METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS (English)

Patent Assignee: ASM MICROCHEMISTRY OY

Author (Inventor): ELMERS KAI-ERIK; HAUKKA SUVI PAIVIKKI; SAANILA VILLE ANTERO; KAIPIO SARI JOHANNA; SOININEN PEKKA JUHA

Priority (Number,Kind,Date): FI 992234 A 19991015; WO 2000FI895 W 20001013

Applic (Number,Kind,Date): AU 200079268 A 20001013

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; H05K-003/00

CA Abstract No: \* 134(21)303342Q; 134(21)304215N; 134(22)318948R

Language of Document: English

Patent (Number,Kind,Date): AU 200110884 A5 20010430

DEPOSITION OF TRANSITION METAL CARBIDES (English)

Patent Assignee: ASM INC

Author (Inventor): ELMERS KAI-ERIK; HAUKKA SUVI P; SAANILA VILLE ANTERO; KAIPIO SARI JOHANNA; SOININEN PEKKA JUHA

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 159799 P 19991015; US 176948 P 20000118; WO 2000US28537 W 20001016

Applic (Number,Kind,Date): AU 200110884 A 20001016

IPC: \* C23C-016/32; H01L-021/00

CA Abstract No: \* 134(13)187114R; 134(21)303341P; 134(21)303342Q; 134(21)304079W; 134(21)304215N; 134(22)318948R

Derwent WPI Acc No: \* C 01-218475; C 01-308262; C 01-308263

Language of Document: English

Patent (Number,Kind,Date): AU 200112082 A5 20010430

METHOD FOR DEPOSITING NANOLAMINATE THIN FILMS ON SENSITIVE SURFACES (English)

Patent Assignee: ASM INC

Author (Inventor): ELMERS KAI-ERIK; HAUKKA SUVI P; SAANILA VILLE ANTERO; KAIPIO SARI

JOHANNA; SOININEN PEKKA JUHA

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 175799 P 19991015; US 176948 P 20000118; WO 2000US28654 W 20001016

Applic (Number,Kind,Date): AU 200112082 A 20001016

IPC: \* H01L-021/768; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(21)303341P; 134(21)303342Q; 134(21)304215N; 134(22)318948R

Derwent WPI Acc No: \* C 01-308262; C 01-308263

Language of Document: English

### Finland (FI)

Patent (Number,Kind,Date): FI 9902233 A 20010416

MENETELMAE LAEHDEKEMIKAALIEN MUUNTAMISEKSI ALCVD-PROSESSISSA FOERFARANDE FOER MODIFIERING AV UTGAANGSAEMNESKEMIKALIERN I EN ALCVD-PROCESS (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELMERS KAI-ERIK (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015

Applic (Number,Kind,Date): FI 992233 A 19991015

IPC: \* C23C-016/44

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 9902234 A 20010416

MENETELMAE SIIRTYMAEMETALLNITRIDIOHUTKALVOJEN KERROSTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING AV OEVERGAANGSMETALLNITRIDTUNNFILMER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELMERS KAI-ERIK (FI); HAUKKA SUVI (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN PEKKA (FI)

Priority (Number,Kind,Date): FI 992234 A 19991015

Applic (Number,Kind,Date): FI 992234 A 19991015

IPC: \* C23C-016/44; C30B-025/02

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 9902235 A 20010416

MENETELMAE ALKUAINEOHUTKALVOJEN KASVATTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING AV ELEMENTTUNNFILMER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELMERS KAI-ERIK (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN PEKKA (FI)

Priority (Number,Kind,Date): FI 992235 A 19991015

Applic (Number,Kind,Date): FI 992235 A 19991015

IPC: \* C23C-016/44; C30B-025/02

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 20000564 A 20010416

MENETELMAE NANOLAMINAATTIEN VALMISTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING AV NANOLAMINATER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY OY (FI)

Author (Inventor): ELMERS KAI-ERIK (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN PEKKA (FI)

Priority (Number,Kind,Date): FI 2000564 A 20000310; FI 992233 A 19991015; FI 992234 A

19991015; FI 992235 A 19991015

Applic (Number,Kind,Date): FI 2000564 A 20000310

IPC: \* C23C-016/30

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 20000564 A0 20000310

MENETELMAE NANOLAMINAATTIEN VALMISTAMISEKSI FOERFARANDE FOER  
FRAMSTAELLNING AV NANOLAMINATER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY OY (FI)

Author (Inventor): ELSERS KAI-ERIK (FI); SAANILA ANTERO VILLE (FI); KAIPIO JOHANNA  
SARI (FI); SOININEN JUHA PEKKA (FI)

Priority (Number,Kind,Date): FI 2000564 A 20000310; FI 992233 A 19991015; FI 992234 A  
19991015; FI 992235 A 19991015

Applic (Number,Kind,Date): FI 2000564 A 20000310

IPC: \* C25D

Language of Document: Finnish; Swedish

### World Intellectual Property Organization, PCT (WO)

Patent (Number,Kind,Date): WO 200115220 A1 20010301

METHOD FOR BOTTOMLESS DEPOSITION OF BARRIER LAYERS IN INTEGRATED CIRCUIT  
METALLIZATION SCHEMES (English)

Patent Assignee: ASM INC (US); SATTA ALESSANDRA (BE); MAEX KAREN (BE); ELSERS KAI  
ERIK (FI); SAANILA VILLE ANTERO (FI); SOININEN PEKKA JUHA (FI); HAUKKA SUVI P (FI)

Author (Inventor): SATTA ALESSANDRA (BE); MAEX KAREN (BE); ELSERS KAI-ERIK (FI);  
SAANILA VILLE ANTERO (FI); SOININEN PEKKA JUHA (FI); HAUKKA SUVI P (FI)

Priority (Number,Kind,Date): US 150486 P 19990824; US 159799 P 19991015; US 176944 P  
20000118

Applic (Number,Kind,Date): WO 2000US23252 A 20000824

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN;  
CR; CU; CZ; DE; DK; DM; DZ; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL;  
IN; IS; JP; KE; KG; KP; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX;  
NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU;  
ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD;  
RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG;  
CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 130000 With international search report; Before expiration of time limit for amending  
the claims and to be republished in the event of the receipt of the amendments

IPC: \* H01L-021/768; H01L-023/532; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(13)187114R; 134(21)304079W; 134(22)318948R; 134(13)187114R

Derwent WPI Acc No: \* C 01-218475; C 01-328500; C 01-328533; C 01-218475

Language of Document: English

Patent (Number,Kind,Date): WO 200127346 A1 20010419

METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS (English)

Patent Assignee: ASM MICROCHEMISTRY OY (FI); ELSERS KAI-ERIK (FI)

Author (Inventor): ELSERS KAI-ERIK (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015

Applic (Number,Kind,Date): WO 2000FI884 A 20001012

Designated States: (National) AE; AG; AL; AM; AT; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH;  
CN; CR; CU; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID;  
IL; IN; IS; JP; KE; KG; KP; KR; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX;  
MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN;  
YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ;

MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 100000 With international search report

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; C30B-035/00

CA Abstract No: \* 134(21)303341P; 134(21)304215N; 134(22)318948R; 134(21)303341P

Derwent WPI Acc No: \* C 01-308262; C 01-328500; C 01-308262

Language of Document: English

Patent (Number,Kind,Date): WO 200127347 A1 20010419

METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS (English)

Patent Assignee: ASM MICROCHEMISTRY OY (FI); ELMERS KAI ERIK (FI); HAUKKA SUVI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Author (Inventor): ELMERS KAI-ERIK (FI); HAUKKA SUVI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number,Kind,Date): FI 992234 A 19991015

Applic (Number,Kind,Date): WO 2000FI895 A 20001013

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; DE; DK; DM; DZ; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 100000 With international search report

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; H05K-003/00

CA Abstract No: \* 134(21)303342Q; 134(21)304215N; 134(22)318948R; 134(21)303342Q

Derwent WPI Acc No: \* C 01-308263; C 01-328500; C 01-308263

Language of Document: English

Patent (Number,Kind,Date): WO 200129280 A1 20010426

DEPOSITION OF TRANSITION METAL CARBIDES (English)

Patent Assignee: ASM INC (US); ELMERS KAI ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Author (Inventor): ELMERS KAI-ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 159799 P 19991015; US 176948 P 20000118

Applic (Number,Kind,Date): WO 2000US28537 A 20001016

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; DE; DK; DM; DZ; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 100000 With international search report

IPC: \* C23C-016/32; H01L-021/00

CA Abstract No: ; 134(22)318948R

Derwent WPI Acc No: ; C 01-328500

Language of Document: English

Patent (Number,Kind,Date): WO 200129891 A1 20010426

CONFORMAL LINING LAYERS FOR DAMASCENE METALLIZATION (English)

Patent Assignee: ASM INC (US)

Author (Inventor): RAAIJMAKERS IVO; HAUKKA SUVI P; GRANNEMAN ERNST H A; SAANILA VILLE ANTERO; SOININEN PEKKA JUHA; ELSERS KAI-ERIK

Priority (Number,Kind,Date): US 159799 P 19991015; US 176944 P 20000118

Applic (Number,Kind,Date): WO 2000US23213 A 20000824

Designated States: (National) JP; KR (Regional) AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE

Filing Details: WO 120000 With international search report; With amended claims and statement

IPC: \* H01L-021/768; H01L-023/532; C23C-016/00

CA Abstract No: ; 134(21)304079W

Derwent WPI Acc No: ; C 01-328533

Language of Document: English

Patent (Number,Kind,Date): WO 200129893 A1 20010426

METHOD FOR DEPOSITING NANOLAMINATE THIN FILMS ON SENSITIVE SURFACES (English)

Patent Assignee: ASM INC (US); ELSERS KAI ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Author (Inventor): ELSERS KAI-ERIK (FI); HAUKKA SUVI P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 175799 P 19991015; US 176948 P 20000118

Applic (Number,Kind,Date): WO 2000US28654 A 20001016

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; DE; DK; DM; DZ; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 130000 With international search report; Before expiration of time limit for amending the claims and to be republished in the event of the receipt of the amendments

IPC: \* H01L-021/768; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(21)303341P; 134(21)303342Q; 134(21)304215N; 134(22)318948R; 134(21)304215N

Derwent WPI Acc No: \* C 01-308262; C 01-308263; C 01-328500

Language of Document: English

#### World Intellectual Property Organization, PCT (WO) - Legal Status

Number	Type	Date	Code	Text
WO 200115220	P	19990824	WO AA	PRIORITY CLAIMED
				US 150486 P 19990824
WO 200115220	P	19991015	WO AA	PRIORITY CLAIMED
				US 159799 P 19991015
WO 200115220	P	20000118	WO AA	PRIORITY CLAIMED
				US 176944 P 20000118
WO 200115220	P	20000824	WO AE	APPLICATION DATA (APPL. DATA)

			WO 2000US23252 A 20000824	
WO 200115220	P	20010301 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
WO 200115220	P	20010301 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
WO 200115220	P	20010301 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO 200115220	P	20010425 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
WO 200115220	P	20010531 WO DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
WO 200127346	P	19991015 WO AA	PRIORITY (PATENT)	
			FI 992233 A 19991015	
WO 200127346	P	20001012 WO AE	APPLICATION DATA	(APPL. DATA)
			WO 2000FI884 A 20001012	
WO 200127346	P	20010419 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE	

DE DK DK DM DZ EE EE ES FI FI GB GD  
 GE GH GM HR HU ID IL IN IS JP KE KG  
 KP KR KR KZ LC LK LR LS LT LU LV  
 MA MD MG MK MN MW MX MZ NO NZ  
 PL PT RO RU SD SE SG SI SK SK SL TJ  
 TM TR TT TZ UA UG US UZ VN YU ZA  
 ZW

WO P 20010419 WO  
 200127346 AL

DESIGNATED COUNTRIES FOR  
 REGIONAL PATENTS CITED IN A  
 PUBLISHED APPLICATION WITH  
 SEARCH REPORT

(DESIGNATED  
 COUNTRIES FOR  
 REGIONAL PATENTS  
 CITED IN A PUBLISHED  
 APPL. WITH SEARCH  
 REPORT)

GH GM KE LS MW MZ SD SL SZ TZ UG  
 ZW AM AZ BY KG KZ MD RU TJ TM AT  
 BE CH CY DE DK ES FI FR GB GR IE IT  
 LU MC NL PT SE BF BJ CF CG CI CM GA  
 GN GW ML MR NE SN TD TG

WO P 20010419 WO  
 200127346 A1

PUBLICATION OF THE  
 INTERNATIONAL APPLICATION WITH  
 THE INTERNATIONAL SEARCH  
 REPORT

(PUB. OF THE  
 INTERNATIONAL APPL.  
 WITH THE  
 INTERNATIONAL  
 SEARCH REPORT)

WO P 20010613 WO  
 200127346 121

EP: THE EPO HAS BEEN INFORMED BY  
 WIPO THAT EP WAS DESIGNATED IN  
 THIS APPLICATION

WO P 20010830 WO  
 200127346 DFPE

REQUEST FOR PRELIMINARY  
 EXAMINATION FILED PRIOR TO  
 EXPIRATION OF 19TH MONTH FROM  
 PRIORITY DATE

WO P 19991015 WO  
 200127347 AA

PRIORITY (PATENT)

FI 992234 A 19991015

WO P 20001013 WO  
 200127347 AE

APPLICATION DATA

(APPL. DATA)

WO 2000FI895 A 20001013

WO P 20010419 WO  
 200127347 AK

DESIGNATED STATES CITED IN A  
 PUBLISHED APPLICATION WITH  
 SEARCH REPORT

(DESIGNATED STATES  
 CITED IN A PUBLISHED  
 APPL. WITH SEARCH  
 REPORT)

AE AG AL AM AT AT AU AZ BA BB BG  
 BR BY BZ CA CH CN CR CU CZ CZ DE  
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 GE GH GM HR HU ID IL IN IS JP KE KG  
 KP KR KR KZ LC LK LR LS LT LU LV  
 MA MD MG MK MN MW MX MZ NO NZ  
 PL PT RO RU SD SE SG SI SK SK SL TJ  
 TM TR TT TZ UA UG US UZ VN YU ZA

ZW

WO P 20010419 WO DESIGNATED COUNTRIES FOR (DESIGNATED  
 200127347 AL REGIONAL PATENTS CITED IN A COUNTRIES FOR  
 PUBLISHED APPLICATION WITH REGIONAL PATENTS  
 SEARCH REPORT CITED IN A PUBLISHED  
 APPL. WITH SEARCH  
 REPORT)

GH GM KE LS MW MZ SD SL SZ TZ UG  
 ZW AM AZ BY KG KZ MD RU TJ TM AT  
 BE CH CY DE DK ES FI FR GB GR IE IT  
 LU MC NL PT SE BF BJ CF CG CI CM GA  
 GN GW ML MR NE SN TD TG

WO P 20010419 WO PUBLICATION OF THE (PUB. OF THE  
 200127347 A1 INTERNATIONAL APPLICATION WITH INTERNATIONAL APPL.  
 THE INTERNATIONAL SEARCH WITH THE  
 REPORT INTERNATIONAL  
 SEARCH REPORT)

WO P 20010613 WO EP: THE EPO HAS BEEN INFORMED BY  
 200127347 121 WIPO THAT EP WAS DESIGNATED IN  
 THIS APPLICATION

WO P 20010816 WO REQUEST FOR PRELIMINARY  
 200127347 DFPE EXAMINATION FILED PRIOR TO  
 EXPIRATION OF 19TH MONTH FROM  
 PRIORITY DATE

WO P 19991015 WO PRIORITY (PATENT)  
 200129280 AA

FI 992233 A 19991015

WO P 19991015 WO PRIORITY (PATENT)  
 200129280 AA

FI 992234 A 19991015

WO P 19991015 WO PRIORITY (PATENT)  
 200129280 AA

FI 992235 A 19991015

WO P 19991015 WO PRIORITY CLAIMED  
 200129280 AA

US 159799 P 19991015

WO P 20000118 WO PRIORITY CLAIMED  
 200129280 AA

US 176948 P 20000118

WO P 20000310 WO PRIORITY (PATENT)  
 200129280 AA

FI 2000564 A 20000310

WO P 20001016 WO APPLICATION DATA (APPL. DATA)  
 200129280 AE

WO 2000US28537 A 20001016

WO P 20010426 WO DESIGNATED STATES CITED IN A (DESIGNATED STATES)

200129280		AK	PUBLISHED APPLICATION WITH SEARCH REPORT	CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
WO 200129280	P	20010426 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
WO 200129280	P	20010426 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO 200129280	P	20010620 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
WO 200129280	P	20010816 WO DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
WO 200129891	P	19991015 WO AA	PRIORITY CLAIMED	
			US 159799 P 19991015	
WO 200129891	P	20000118 WO AA	PRIORITY CLAIMED	
			US 176944 P 20000118	
WO 200129891	P	20000824 WO AE	APPLICATION DATA	(APPL. DATA)
			WO 2000US23213 A 20000824	
WO 200129891	P	20010426 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)

			JP KR	
○	WO 200129891	P	20010426 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT  (DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE	
	WO 200129891	P	20010426 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT  (PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
	WO 200129891	P	20010620 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION
	WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)
			FI 992233 A 19991015	
	WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)
			FI 992234 A 19991015	
○	WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)
			FI 992235 A 19991015	
	WO 200129893	P	19991015 WO AA	PRIORITY CLAIMED
			US 175799 P 19991015	
	WO 200129893	P	20000118 WO AA	PRIORITY CLAIMED
			US 176948 P 20000118	
	WO 200129893	P	20000310 WO AA	PRIORITY (PATENT)
			FI 2000564 A 20000310	
	WO 200129893	P	20001016 WO AE	APPLICATION DATA  (APPL. DATA)
			WO 2000US28654 A 20001016	
	WO 200129893	P	20010426 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT  (DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG	

KP KR KR KZ LC LK LR LS LT LU LV  
MA MD MG MK MN MW MX MZ NO NZ  
PL PT RO RU SD SE SG SI SK SK SL TJ  
TM TR TT TZ UA UG US UZ VN YU ZA  
ZW

WO P 20010426 WO  
200129893 AL

DESIGNATED COUNTRIES FOR  
REGIONAL PATENTS CITED IN A  
PUBLISHED APPLICATION WITH  
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(DESIGNATED  
COUNTRIES FOR  
REGIONAL PATENTS  
CITED IN A PUBLISHED  
APPL. WITH SEARCH  
REPORT)

GH GM KE LS MW MZ SD SL SZ TZ UG  
ZW AM AZ BY KG KZ MD RU TJ TM AT  
BE CH CY DE DK ES FI FR GB GR IE IT  
LU MC NL PT SE BF BJ CF CG CI CM GA  
GN GW ML MR NE SN TD TG

WO P 20010426 WO  
200129893 A1

PUBLICATION OF THE  
INTERNATIONAL APPLICATION WITH  
THE INTERNATIONAL SEARCH  
REPORT

(PUB. OF THE  
INTERNATIONAL APPL.  
WITH THE  
INTERNATIONAL  
SEARCH REPORT)

WO P 20010620 WO  
200129893 121

EP: THE EPO HAS BEEN INFORMED BY  
WIPO THAT EP WAS DESIGNATED IN  
THIS APPLICATION

WO P 20010802 WO  
200129893 DFPE

REQUEST FOR PRELIMINARY  
EXAMINATION FILED PRIOR TO  
EXPIRATION OF 19TH MONTH FROM  
PRIORITY DATE

INPADOC/Family and Legal Status

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